Topological Defects in Size-Dispersed Solids

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(submitted to Phys. Rev. Letters 7 Jan 2000)

Abstract

We study the behavior of the topological defects in the inherent structures of a two-dimensional binary Lennard-Jones system as the size dispersity varies. We find that topological defects arising from the particle size dispersity are responsible for destabilizing the solid as follows: (i) for particle density $\rho \leq 0.9$, the solid melts through intermediate states of decreasing hexatic order arising from the proliferation of unbounded dislocations, (ii) for $\rho > 0.9$, the dislocations form grain boundaries, dividing the system into micro-crystallites and destroying the translational and orientational order.

Topological defects play a crucial role in melting of a solid, especially in two dimensions. In two dimensions (2D) these defects, present in bound pairs at low temperature solid phase, are believed to unbind and destroy the crystalline order as temperature is raised causing melting [1]. Like temperature, size-dispersity (inhomogeneity in particle size) *disfavors* crystalline order, and can even convert a solid to a liquid [2,3]. Here we study the defect morphology in the inherent structures of a 2D Lennard-Jones system with a bimodal distribution of particle sizes.

We simulate $N = 10^4$ particles interacting with a truncated "shifted-force Lennard-Jones" pair-potential in 2D. We choose half the particles to be smaller than the rest, and define the size dispersity Δ to be the ratio of the difference in their sizes to the mean size. We start by placing the particles randomly on the sites of a triangular lattice, embedded in a rectangular box of edges L_x and L_y with aspect ratio $L_x/L_y = \sqrt{3}/2$ (to accommodate close-pack hexagonal structure without distortion). We apply periodic boundary condition and use the velocity Verlet method to integrate Newton's equation of motion. Units are set by choosing the mass of the particles and the Lennard-Jones (LJ) energy and length scales to be unity. The density ρ is the ratio of the area occupied by the particles to the box area.

We equilibrate a state, defined by (ρ, Δ), at a constant temperature $T = 1$ using Berendsen's thermostat; at this temperature the 2D solid can form for low enough dispersity. We run our simulation at constant energy until the temperature T, the pressure P, and the energy E stabilize with less than 1% fluctuation (typically for 2×10^5 time steps, where the time step is 0.01 in LJ units). We also check that the average particle displacement is at least a few times the average particle size. To obtain higher density states, we increase ρ in steps of 0.01 from 0.85 (liquid state) to 1.05 by gradually compressing the box, keeping the aspect ratio fixed, and equilibrating the system at each of these densities.

We perform defect analysis on 100 equilibrated configurations for each of the state points (ρ, Δ). Clear identification of geometrical defects is difficult in simulations due to the presence of many "virtual defects" which arise because of vibrational excitations. To overcome this difficulty, we analyze the inherent structure of each configuration [4], obtained by removing the vibrational excitations—or equivalently by minimizing (locally) the potential energy using the conjugate gradient method.

In order to find the defects, we construct a Voronoi cell around each particle, thereby uniquely defining its nearest neighbors. The ordered close-packed structure of the 2D solid is hexagonal, so each particle i at position $\mathbf{r}_i$ has $n_i = 6$ neighbors. A defect arises when a particle has $n_i \neq 6$, which generates a "topological charge" $q_i \equiv n_i - 6$ [5]. Defects which are nearest neighbors are grouped as defect clusters with total charge $Q \equiv \sum_i q_i$ and total

dipole moment $\mathbf{P} \equiv \sum_i \mathbf{r}_i q_i$, where the sum is over all defects i in the cluster. Figure 1 shows an example of defects in an otherwise ideal triangular lattice.

We find that the defects fall into three categories: (i) *Monopoles.* Clusters with $Q \neq 0$. The simplest case is a disclination—a size-one cluster (Fig. 1a). (ii) *Dipoles.* Clusters with $\mathbf{P} \neq 0$. The simplest case is a dislocation, a size-two cluster (Figs. 1a and 1b), composed of a "bound pair" of neighboring defects of opposite charge. (iii) *Blobs.* Clusters with $Q = \mathbf{P} = 0$. The most common case is a quadrupole (Fig. 1a) made of a "bound pair" of neighboring dislocations with oppositely-oriented dipole moments (see, e.g., [6, 7]).

Figure 2 shows typical snapshots of the inherent structure at $\rho = 0.9$ for three values of Δ. The corresponding phase points (ρ, Δ) represent solid, hexatic and liquid phases [3]. In the low-dispersity solid phase [Figs. 2a and 2b], defects occur mostly in the form of blobs (quadrupoles). Such defects, being without charge or dipole moment, cause little distortion in the nearby order and so are energetically inexpensive. We find that the defects in the inherent structure of the solid phase aggregate to form domains separated by nearly defect-free regions, suggesting that there is an effective attraction between defects. This effective attraction may arise from packing constraints since in dense packing, formation of a local large-amplitude defect is improbable. As Δ increases, more defects in the form of dipoles are created.

At large defect density, free dislocations appear. Figure 2c shows their presence, in the hexatic phase. A dislocation destroys the long-range translational order as it introduces an extra half row (Fig. 1b) that can only terminate in another dislocation with equal but opposite dipole moment. Translational order is destroyed over the range of separation of the dislocation pair [1]. Dislocations, however, retain orientational order. We find in configurations such as Fig. 2c that 2D translational order is lost (due to the abundance of dipoles). However, orientational order shows an algebraic decay—the characteristic features of a hexatic phase [1]. The system breaks up into crystalline patches of finite length ξ_t (the translational correlation length) which are shifted but not rotated with respect to one another, so the range of orientational correlation ξ_6 far exceeds ξ_t. On further increasing

Δ, more defects are created: many monopoles appear which destroy the orientational order and the system melts [Fig. 2d] (see [6, 7]).

In the hexatic phase, we find a steep increase in the number of dipoles (Fig. 3a) between Δ_{SH} (the solid-hexatic transition value for Δ) and Δ_{HL} (the hexatic-liquid transition value for Δ). Also, we detect a gentler increase in the number of monopoles as the hexatic-liquid transition at $\Delta = \Delta_{\mathrm{HL}}$ is approached. KTHNY theory [1] predicts that in the liquid phase, the orientational correlation function $C_6(r)$ decays exponentially, $C_6(r) \sim e^{-r/\xi_6}$, with an orientational correlation length ξ_6 that diverges as the liquid-hexatic transition is approached [1]. Figure 3b reveals a rapid increase of ξ_6 as the liquid-hexatic phase boundary is approached from the liquid side.

Figures 4b–d show typical snapshots of the inherent structure at $\rho = 1.0$, for $\Delta = 0.04$, 0.1 and 0.12. A first order solid-liquid transition is found at the value $\Delta_{\mathrm{SL}} \approx 0.1$ [3], the solid-liquid transition value for Δ. Our defect analysis shows that for $\Delta < \Delta_{\mathrm{SL}}$, there are free dislocations, and near the transition these defects line up in "strings" to form long chains of large-angle grain boundaries (Fig. 4c). As $\Delta \to \Delta_{\mathrm{SL}}$, these chains percolate, fragmenting the system into micro-crystallites rotated with respect to each other. Thus the grain boundaries simultaneously destroy both the translational and the rotational order. In the theory of grain-boundary-induced melting [8, 9], the Landau free-energy expansion yields a first-order solid-liquid transition with the absence of any hexatic phase. We find that the formation of defects and the proliferation of grain boundaries occurs abruptly at $\Delta_{\mathrm{SL}} \approx 0.1$. Within the resolution of our simulations, we do not see any hexatic phase [3].

In summary, we have seen that size-dispersity induces topological defects which in turn destroy crystalline order, and that the mechanism of dispersity-induced melting displays surprising parallels with the mechanism proposed for the case of temperature-induced melting. Depending on the value of ρ, dispersity-induced melting can be either a first-order transition or a continuous transition (with an intervening hexatic phase), and the defect morphologies display completely different behavior in the two cases.

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FIG. 1.   Identification of defects taken from our simulated system. Neutral ($n_i = 6$) particles are shown as dots. Solid squares and triangles denote defects, with $n_i = 7$ ($q = +1$) and $n_i = 5$ ($q = -1$) respectively. Neighboring defects form different types of defect clusters as explained below. (a) The large open square denotes a positive monopole. It represents a cluster of size one, which is the positive defect it contains, thus it is a disclination. The large open triangle denotes a negative monopole. It represents a cluster of size three, which consists of two negative and one positive defects. The arrows denote dipoles; all but the largest arrow (pointing "East") represent clusters of size two, and hence all but one dipole are dislocations. The largest arrow denotes a dipole, the vector sum of two adjacent disclinations forming a cluster of size four with a non-zero net dipole moment. Finally, the parallelogram contains a cluster of two $n_i = 5$ ($q = -1$) and two $n_i = 7$ ($q = +1$) defects with zero net charge and zero net dipole moment (hence a quadrupole). (b) A dislocation dipole (solid arrow). Also shown is the corresponding Burger's vector (dashed arrow), as the vector needed to close an equilateral (in this case 3×3) contour around the dislocation. The thin solid line marks the extra row which ends at the dipole. The length of the dipole arrow represents the magnitude of the dipole $\mathbf{P}$, proportional to the length of the Burger's vector.

FIG. 2. Defects of four different $\rho = 0.9$ configurations. The symbols used for the defects are same as in Figure 1. (a) A $\Delta = 0.04$ configuration; this configuration is in the solid phase. The magnified portion includes two dislocations and a cluster of size 10 (encircled by the dashed line) with an overall dipole moment. (b) The inherent structure for the same $\Delta = 0.04$ configuration. Most defects in (a) and (b) form quadrupoles, and some form dipoles. Notice that upon forming the inherent structure of a configuration, the particles with six neighbors move locally to form an ordered triangular lattice structure. Also many of the defect clusters, mostly low energy quadrupoles and some dipoles and monopoles, disappear. There remain only a few defect clusters, topological defects that cannot be annihilated by local translations performed in generating the inherent structure; e.g. in the magnified region, most of the defects have disappeared; there remains only one dislocation, the vector sum of the three previous dipoles. (c) Inherent structure for $\Delta = 0.06$ configuration (in the hexatic phase). The arrows denote dipoles. Note that free dislocation dipoles appear. (d) Inherent structure for $\Delta = 0.09$ configuration (in the liquid phase). Many disclination monopole defects, shown as open triangles and squares, appear. For clarity, individual defect particles and blobs (including therefore quadrupoles) are not shown in c and d. Dipole clusters are represented by the dipole vector for each cluster.

FIG. 3. (a) The number of different defect clusters as a function of Δ along the $\rho = 0.9$ isochore. There is first a ten-fold increase in the number of *dipoles* associated with the solid-hexatic transition Δ_{SH}. Then a large increase in the number of *monopoles* occurs near the hexatic-liquid transition Δ_{HL}. (b) Orientational correlation length ξ_6 as a function of Δ along the same $\rho = 0.9$ isochore. Upon approaching the hexatic phase from the liquid phase (i.e., as $\Delta \to 0.06^+$), ξ_6 diverges.

FIG. 4. Defects of the $\rho = 1.0$ system. (a) A $\Delta = 0.04$ configuration, which is in the solid phase. The defects are magnified in the insets. This configuration contains only two dipoles and one low energy quadrupole. Note that the leftmost and rightmost defects (two dipoles) cancel, a feature characteristic of the solid phase. (b) The quadrupole disappears upon generating the inherent structure. (c) Inherent structure for a $\Delta = 0.095$ configuration which is in the solid phase near the melting point. (d) Inherent structure for a $\Delta = 0.115$ configuration, which is in the liquid phase. Note that the defects form lines (grain boundaries) that partition the system into sub-regions of solid order (micro-crystallites). Unlike the liquid in Fig. 2d, there are few disclination monopoles. What destroys the solid order is the existence of the grain boundaries, while in Fig. 2d what destroys the solid order is the existence of both free dislocations and free disclinations.

(a)

(b)

(c)

9

(d)

(a)

Number of defect clusters

Δ_{SH} Δ_{HL}

dipoles

monopoles

quadrupoles

Δ

(b)

Orientational correlation length

ρ=0.9

Δ

(d)